

965,358



PATENT SPECIFICATION

DRAWINGS ATTACHED

965,358

Date of Application and filing Complete Specification: Dec. 21, 1962.

No. 48310/62.

Application made in Netherlands (No. 272941) on Dec. 27, 1961.

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Index at acceptance:—C1 A (1B1G, 1C1, 1C2, 1D, E2X) ; B1 L3

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COMPLETE SPECIFICATION

Process for the Separation of Acid Components from a Mixture

ERRATA

SPECIFICATION No. 965,358
Amendment No. 1

Page 4, line 97, for "maner," read "manner,"
Page 4, line 101, for "neccssarily" read
"necessarily"

THE PATENT OFFICE
26th August 1966

ethanolamine, diethanolamine, dipropanolamine and especially diisopropanolamine), a
25 cyclotetramethylene sulphone (e.g. tetramethylene sulphone itself or a derivative thereof) or a mixture of an alkanolamine and a cyclotetramethylene sulphone, the solvent removing the said acid components. The
30 solvent and starting mixture are preferably contacted countercurrently in the separation zone (e.g. an extraction zone or an absorption zone).

35 As a rule the separation of the acid components need not be complete; generally a product has to be supplied which meets a certain specification and therefore does not contain more acid components than corresponds within the limits mentioned in the said specification.
40

The purified product and the charged solvent are withdrawn from the separation zone. The charged solvent is regenerated by passing it to a stripper in which it is at least substantially

is essential.

The invention provides an economic method of carrying out the process described, so that it can be carried out continuously under optimum, or substantially optimum, conditions as regards the use of solvent and heating; under these conditions the risk of corrosion is also reduced, since the stripper can usually be operated at lower temperatures. In the process according to the invention the residual content of acid components in the purified product can be generally kept very low.

According to the invention, in a process of the kind specified the amount of solvent supplied to the separation zone is controlled in dependence on the residual content of acid components (for instance the hydrogen sulphide content) in the product already purified (or in dependence also on the quantity of acid components, for instance the quantity of hydrogen sulphide, supplied to the separation zone per unit of time) such that the quantity of solvent

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Process for the Separation of Acid Components from a Mixture

- We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a Company organised under the Laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- 10 This invention related to a process for the separation of acid components, such as hydrogen sulphide, carbon dioxide and carbon oxy-sulphide, from gases or liquids such as hydrogen, nitrogen, oxygen and light hydrocarbons, in general from gaseous or liquid mixtures which are not substantially soluble in water or aqueous liquids. The process is of the kind in which the separation is effected by contacting the starting mixture with an aqueous solvent for the acid components, such as an aqueous solution containing potassium phosphate (K_3PO_4), an alkanolamine (e.g. monoethanolamine, diethanolamine, dipropanolamine and especially diisopropanolamine), a cyclotetramethylene sulphone (e.g. tetramethylene sulphone itself or a derivative thereof) or a mixture of an alkanolamine and a cyclotetramethylene sulphone, the solvent removing the said acid components. The solvent and starting mixture are preferably contacted countercurrently in the separation zone (e.g. an extraction zone or an absorption zone).
- As a rule the separation of the acid components need not be complete; generally a product has to be supplied which meets a certain specification and therefore does not contain more acid components than corresponds within the limits mentioned in the said specification.
- The purified product and the charged solvent are withdrawn from the separation zone. The charged solvent is regenerated by passing it to a stripper in which it is at least substantially freed from the absorbed components by heating. The whole or most of the solvent thus regenerated is returned to the separation zone, usually after being previously cooled to a suitable lower temperature by heat exchange and/or cooling.
- The process described above is well-known and has been successfully used in practice for many years. Hitherto the process has been carried out with the use of a relatively large, constant stream of solvent and a relatively large, constant supply of heat (usually in the form of steam) to the stripper, in order to ensure that under all circumstances (thus for example independently of the composition of the starting mixture to be treated) a product is supplied of which the residual content of acid components is invariably below the specification limits.
- However, such a mode of operation is uneconomic, as much more steam is used for heating, and solvent for the separation, than is essential.
- The invention provides an economic method of carrying out the process described, so that it can be carried out continuously under optimum, or substantially optimum, conditions as regards the use of solvent and heating; under these conditions the risk of corrosion is also reduced, since the stripper can usually be operated at lower temperatures. In the process according to the invention the residual content of acid components in the purified product can be generally kept very low.
- According to the invention, in a process of the kind specified the amount of solvent supplied to the separation zone is controlled in dependence on the residual content of acid components (for instance the hydrogen sulphide content) in the product already purified (or in dependence also on the quantity of acid components, for instance the quantity of hydrogen sulphide, supplied to the separation zone, per unit of time) such that the quantity of solvent

supplied increases with increasing content of acid components and vice versa, while the heat supplied to the bottom of the stripper is controlled in dependence on the temperature at the top part of the stripper such that the supply of heat increases with a decreasing temperature at the top part of the stripper to maintain that temperature at least approximately at a desired value.

This desired value of the temperature is preferably set, and if necessary varied, according to the pressure in the stripper and the permissible content of acid components (for instance the permissible hydrogen sulphite content) of the returned solvent and/or of the purified product; the content of acid components in the returned solvent is directly related to the permissible residual content of these components in the purified product.

The invention may be performed in various ways and a specific embodiment will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a flow diagram of the present process; and

Figure 2 shows a detail of the control system.

In the process shown in Figure 1 a gas mixture containing light hydrocarbons and hydrogen sulphide, and in which hydrogen, nitrogen and similar gases may also be present, is led through a line 1 to the bottom of an absorption zone 2 (an absorption column which may be provided with trays). To the top part of this column an aqueous solvent (in the present instance an aqueous solution of diisopropanolamine) is supplied through a line 3. The solvent is passed through the column countercurrently with the rising gas as a consequence of which the hydrogen sulphide is at least substantially removed from the gas. The purified gas passes overhead through a line 4 and the charged solvent is removed at the bottom through a line 5. The charged solvent passes through a heat exchanger 6 and is introduced at the top part of a stripper 7 (likewise a column which may be provided with trays). In the stripper the hydrogen sulphide is at least substantially separated from the solvent by heating. The stripped solvent leaves the stripper at the bottom and is returned to the absorption zone by means of a pump 8, through the line 3, via a cooler 9 after passing through the above-mentioned heat exchanger 6.

Hydrogen sulphide, together with water vapour, leaves the top part of the stripper through a line 10. This mixture passes through a condenser 11 and a separator 12. The condensed water is separated in the separator and all or some of it may be led through a line 13 to the top part of the stripper 7. The gas leaves the separator through a line 14; if desired, the condensed water, or a portion thereof, may be passed off through a line 15, which measure may

or may not be combined with supplying fresh water to the stripper 7. This water may be supplied, for example, by injecting condensed steam into the line 13.

Heat is supplied to the bottom part of the stripper 7 by reboiling; to this end steam is supplied through a line 16 to a reboiler 17.

The flow scheme described above is well-known. In the known mode of operation a constant circulation of solvent is applied via the line 3, viz. an excessive circulation in order to ensure that under all circumstances the hydrogen sulphide is removed to a sufficient extent from the gas to be purified. As a consequence of this mode of operation more hydrogen sulphide is usually separated from the gas than is strictly necessary, as the process is set to the most unfavourable conditions which could ever occur. Consequently, on the one hand there is continuous relatively heavy loss of solvent, and on the other an excessive amount of steam is continuously consumed for the regeneration of the solvent. In fact, the quantity of steam supplied at 16 (or, as the case may be, the quantity of heat supplied or the quantity of condensate formed in the reboiler 17 from the steam) is kept constant; this quantity of steam is such that the solvent is always freed from the hydrogen sulphide to such an extent that it can work satisfactorily under the most unfavourable feed conditions, even when such unfavourable conditions do not occur; this means that the solvent is usually freed from hydrogen sulphide to a much larger extent than is necessary. In general, the steam consumption is therefore excessively high for two reasons, viz. excessive solvent circulation and excessive freeing from hydrogen sulphide.

Figure 1 also shows the manner in which in the known process the steam consumption can be kept constant by means of a control valve 18 and a control and measuring device 19; the device 19 measures the quantity of steam passing through the line 16, observes deviations from the desired, preset amount of steam and adjusts the control valve 18 correspondingly. The same remarks apply when, instead of the quantity of steam the quantity of condensate formed from this steam in the reboiler is kept constant. Instead of measuring the quantity of steam, the quantity of heat supplied to the reboiler may be measured; in this case a heat measuring device is used instead of a flowmeter. Heat-measuring can be conveniently used when heating is carried out by means of a non-condensing heating medium, for example hot oil.

In the known process the solvent circulation stream is kept constant in a similar manner. In this stream there is provided a control valve 20 which is operated by a measuring and control device 21. This device measures the flow rate and adjusts the valve in depen-

dence thereon in such a way as to keep the flow rate at a preset constant value.

The object of the invention is to carry out the process more economically by controlling the process in such a manner that the purified gas invariably just meets the specification covering the permissible residual content of acid components, viz. hydrogen sulphide.

Assuming for the moment that the quantity of hydrogen sulphide supplied per unit of time does not show excessively large variations, the method of control is as follows. The residual content of hydrogen sulphide in the purified gases is measured by means of a suitable instrument 22 (for instance an instrument known as an "Ionoflux" (trade mark)). This residual content should not exceed a certain value, which may vary from case to case; in general, the permissible content depends upon the requirements of the user.

The actual value measured by the instrument 22 is compared in a controller 23 with the desired value set at this controller at 24, the latter value conveniently being somewhat lower than the value corresponding to the said maximum permissible residual content. The signal of the controller 23 is passed to the control device 21 and varies the desired value setting of this device. Thus in contrast to the preset constant desired value of the flow rate of the circulating solvent in the known process, in the present invention that desired value is varied via the measuring instrument 22 and the controller 23 in such a way that the residual content of hydrogen sulphide in the purified gases does not exceed the permissible maximum.

The control method operates in such a manner that the solvent circulation increases with increasing concentration of hydrogen sulphide in the purified gas and vice versa.

If considerable variations are to be expected in the quantity of hydrogen sulphide supplied with the feed per unit of time, the control method may be combined with a control technique based on the quantity of hydrogen sulphide present in the feed and supplied to the absorption zone per unit of time. This amount of hydrogen sulphide (i.e. the hydrogen sulphide concentration in the feed multiplied by the flow rate of the feed) is determined by an instrument 25; the actual value thus measured is passed to a control device 26, the signal of which also controls the desired value setting of the control device 21.

The set point of the control device 21 may therefore be controlled either by the signal originating from 23 or by a suitable combination (for instance the sum) of the signals originating from 23 and 26.

The maximum permissible residual content of hydrogen sulphide in the purified gases also determines, at least substantially, the maximum residual content of hydrogen sulphide which may be allowed in the stripped solvent.

In order to keep the steam consumption as low as possible, as already remarked, the removal of hydrogen sulphide should not exceed, or not much exceed, that required to provide the said maximum permissible residual content in the purified solvent. Of course the stripped solvent should not contain appreciably more than the maximum permissible residual content for a substantial period, as in that case the absorption in the column 2 would no longer take place in the proper manner.

Instead of keeping the steam consumption constant, as was formerly the case, this consumption is now controlled in such a way that the concentration of acid components, viz. hydrogen sulphide in the present embodiment, of the stripped solvent does not exceed the maximum permissible concentration and is always kept very near to the latter concentration. According to the invention this control is accomplished in dependence on the temperature measured at the top part of the stripper since, surprisingly, it has been found that this top temperature is a very sensitive indication of the hydrogen sulphide concentration in the stripped solvent.

In order to carry out the control method the top temperature is measured by an instrument 27. The actual value measured is passed to a controller 28 and is there compared with the desired value for the top temperature, viz. the value of the top temperature at which the stripped solvent has the said maximum permissible residual concentration (or a somewhat lower concentration) of hydrogen sulphide. The signal of the controller 28 controls the desired value setting of the control device 19 described above. In this way there is supplied precisely the minimum amount of steam required to effect the desired degree of stripping of the solvent.

In this connection it should be noted that the desired value of the temperature set at the controller 28 should be changed if for any reason the degree of stripping in the column 7 has to be increased or reduced (a higher temperature being required for increased stripping).

The relationship between the top temperature of the stripper and the hydrogen sulphide content of the stripped solvent is also found to be dependent on the pressure in the stripping column; this pressure need not always be constant and may depend on such factors as the quantity of hydrogen sulphide removed from the solvent and on disturbances caused by the installation in which the hydrogen sulphide produced is being worked up.

This dependence may be eliminated from the control process by keeping the pressure in the column constant. A control device for ensuring a constant pressure may be provided in the line 10 in a known manner.

However, it is preferred not to apply a

constant pressure control. If there is constant pressure control the pressure in the stripper will almost continuously be higher than would be the case without this control and the temperature set on the controller 28 should be correspondingly higher; as a result the heating of the stripper column would become less economic and there would be a greater risk of corrosion caused by hydrogen sulphide.

In order to obviate this drawback, the pressure is measured by means of a pressure meter and the desired temperature, viz. the temperature set at the controller 28, is varied according to the experimentally ascertained relationship between this temperature and the pressure in the stripper for each desired degree of stripping of the solvent. The varying, desired temperature set at the controller 28 may be adjusted by hand when pressure conditions in the stripper only change slowly. With more rapid variations, the value of the pressure measured by a pressure gauge 29 may be passed as a signal to a device 30 to which device the desired degree of stripping (for example also in the form of a variable signal or by adjustment of a variable magnitude of this device) is additionally passed at 31.

The said device supplies a signal by which the set point of the controller 28 (the desired value of the temperature) is adjusted.

Figure 2 shows a special embodiment of the above-mentioned control system for a case in which the pressure is not constant. The temperature measuring device 27 is equipped with a small vessel (probe) 27¹, which is situated inside the column 7 and is exposed to the temperature in the top part of this column. Inside the probe there is a material which is partly in liquid and partly in vapour phase and which has a vapour pressure curve which is the same as, or similar to, the vapour pressure curve of the mixture in the top part of the stripper, or which at least runs nearly parallel to the latter curve. In the present case this material may be, for example, water. The device 27 supplies a pressure which corresponds to the vapour pressure of the liquid in the probe 27¹ at the top temperature in the stripper. In a device 32 (for example a pneumatic relay circuit) this pressure is compared with the actual pressure prevailing in the column which is measured by the gauge 29. The device 32 supplies a controller 33 with a signal the magnitude of which depends on the ratio of the two pressures just mentioned. In the controller 33 this signal is compared with the desired value of this ratio, which is supplied to or set at 34. The controller sends a signal to the control device 19 described above.

If the ratio of the two pressures corresponds to the desired value set at the controller 34, the set point of the control device 19 is

unchanged. If, however, the pressure measured by 29 is higher than that corresponding to the said set ratio, then the desired value set point of the device 19 is shifted in such a way that a larger amount of steam is supplied; at a lower pressure the quantity of steam is reduced.

The desired value of the said ratio set at 34 may be varied; in this way it is possible to influence the desired degree of stripping of the solvent.

When applying the control system shown in Figure 2 to the process shown schematically in Figure 1, the devices 30 and 28 in Figure 1 are replaced by the devices 32 and 33, and use is also made of the special devices 27 and 27¹ for measuring the temperature.

For the sake of simplicity, in the above description only hydrogen sulphide was mentioned, if other acid components, for example carbon dioxide, or a combination of acid components, for instance hydrogen sulphide and carbon dioxide, have to be removed, the above applies in the same way as far as the separation, stripping, measuring and control of such other components or such combinations of components is concerned.

The diagram given is one of numerous possible embodiments which may differ in detail. The control 20, for example, need not be effected by means of a valve but may also be effected in another manner, for instance by controlling the pumping rate of the pump 8. Instead of a control system involving a control valve in a line, a control system with a bypass line may be used. Heating does not necessarily have to be effected by means of steam, but may be carried out, for example, with hot oil. It is not necessary to recirculate all the solvent from the stripper 7, but a relatively small solvent stream may be drawn off and replaced by fresh solvent. If desired, absorption in the column 2 may be in the form of rectifying absorption.

The separation zone may consist of more than one column, in which columns different starting mixtures may be treated, if desired, the various solvent streams being stripped in a single stripper. The stripping zone also may consist of a number of stripping columns.

WHAT WE CLAIM IS:—

1. A process for the separation of acid components from a mixture which is not appreciably soluble in water or aqueous liquids, by means of an aqueous solvent for these components, which comprises contacting the starting mixture and the solvent in a separation zone, withdrawing from this zone the purified product and the charged solvent, heating the charged solvent in a stripper to free it at least substantially from the absorbed components and returning the stripped solvent to the separation zone, and which includes controlling the quantity of solvent supplied to the separation zone in dependence on the

- residual content of acid components in the purified product (or in dependence also on the amount of acid components supplied to the separation zone per unit of time), such
5 that the quantity of solvent supplied increases with increasing content of acid components and vice versa, and controlling the supply of heat to the bottom part of the stripper in
10 dependence on the temperature at the top part of the stripper such that the supply of heat increases with a decreasing temperature at the top part of the stripper to maintain
that temperature at least approximately at a desired value.
- 15 2. A process as claimed in Claim 1 in which the desired value of the said temperature is determined according to the pressure in the stripper and the permissible content of acid components in the returned solvent or the
20 purified product.
3. A process as claimed in Claim 1 or 2 in which the temperature at the top part of the stripper is measured by means of a probe
containing a material having a vapour pressure curve which is the same as, or similar to,
25 the vapour pressure curve of the mixture at the top part of the stripper, the pressure prevailing in the stripper is compared with the vapour pressure of the liquid in the probe,
30 and the heat supplied to the stripper is controlled in dependence on that comparison.
4. A process for the separation of acid components from a mixture, substantially as described with reference to Figure 1 of the
35 accompanying drawings.
5. A process for the separation of acid components from a mixture, substantially as described with reference to Figure 1 as
40 modified in accordance with Figure 2 of the accompanying drawings.
6. A mixture at least partly freed from acid components thereof by a process as claimed in any of the preceding claims.
- KILBURN & STRODE,
Chartered Patent Agents,
Agents for the Applicants.

965358

COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

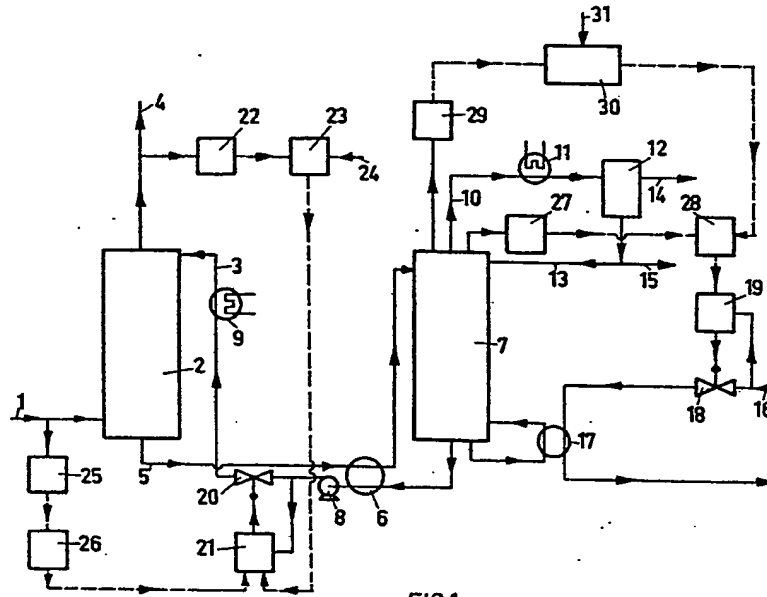


FIG.1

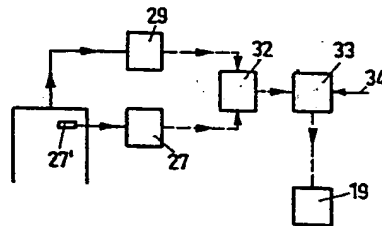


FIG.2

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